

## 5. POTENTIAL FOR HUMAN EXPOSURE

### 5.1 OVERVIEW

Benzene is released to the environment by both natural and industrial sources, although the anthropogenic emissions are undoubtedly the most important. Emissions of benzene to the atmosphere result from gasoline vapors, auto exhaust, and chemical production and user facilities. EPA's estimate of nationwide benzene atmospheric emissions from various sources was  $\approx 34,000$  metric tons/year (EPA 1989d). According to the Toxics Release Inventory, releases to the air from manufacturing and processing facilities were  $\approx 10.2$  million pounds ( $\approx 4,600$  metric tons) in 1993 (TRI93 1995). Releases to air accounted for about 96.2% of the total industry-related releases to the environment (TRI93 1995). Benzene is released to water and soil from industrial discharges, landfill leachate, and gasoline leaks from underground storage tanks.

Chemical degradation reactions, primarily reaction with hydroxyl radicals, limit the atmospheric residence time of benzene to only a few days, and possibly to only a few hours. Benzene released to soil or waterways is subject to volatilization, photooxidation, and biodegradation. Biodegradation, principally under aerobic conditions, is the most important environmental fate process for water- and soil-associated benzene.

Benzene is ubiquitous in the atmosphere. It has been identified in air samples of both rural and urban environments and in indoor air. Although a large volume of benzene is released to the environment, environmental levels are low because of efficient removal and degradation processes. Benzene partitions mainly into air (99.9%) and inhalation is the dominant pathway of human exposure; inhalation accounts for more than 99% of the total daily intake of benzene (Hattemer-Frey et al. 1990). The general population is exposed to benzene primarily by tobacco smoke (both active and passive smoking) and by inhaling contaminated air (particularly in areas with heavy motor vehicle traffic and around filling stations). Air around manufacturing plants that produce or use benzene and air around landfills and hazardous waste sites that contain benzene are additional sources of exposure. Exposure to benzene can also result from ingestion of contaminated food or water. Use of contaminated tap water for cooking, showering, etc., can also be a source of inhalation exposure since benzene can volatilize from water. Compared to inhalation, dermal exposure probably accounts for a minor portion of the total exposure of the general population. The magnitude of exposure is greatest for those

individuals occupationally exposed to benzene; however, a far greater number of individuals are exposed as a result of benzene released from gasoline filling stations, from smoking tobacco products, and from auto exhaust. Smoking was found to be the largest anthropogenic source of background human exposure to benzene (Hattermer-Frey et al. 1990).

Benzene has been identified in at least 816 of the 1,428 current or former NPL hazardous waste sites (HazDat 1996). However, the number of sites evaluated for benzene is not known. The frequency of these sites within the United States can be seen in Figure 5-1. Of these sites, 813 are located in the United States, 1 is located in the Virgin Islands, and 2 are located in the Commonwealth of Puerto Rico (not shown).

## **5.2 RELEASES TO THE ENVIRONMENT**

### **5.2.1 Air**

Benzene is released into the atmosphere from both natural and industrial sources. Natural sources include crude oil seeps, forest fires, and plant volatiles (Brief et al. 1980; Graedel 1978). Major anthropogenic sources of benzene include environmental tobacco smoke, automobile exhaust, automobile refueling operations, and industrial emissions. Using source exposure modeling, it was estimated that benzene emissions were highest from coke oven blast furnaces (Edgerton and Shah 1992). Other sources that contributed to emissions of benzene are automobiles, petrochemical industries, waste water treatment plants, and petroleum industries (Edgerton and Shah 1992). Under California legislation, the City of Los Angeles prepared air toxics emissions inventories at its four waste water treatment plants. The two facilities with greater potential to emit toxics had benzene emission rates of 163 and 108 kg/year. The other facilities had benzene emission rates of 1 and 3 kg/year (Mayer et al. 1994). EPA (1989e) estimates of recent nationwide benzene atmospheric emissions, in metric tons/year (kkg/year), from various industrial sources include: (1) coke by-product recovery plants (17,000 kkg/year), (2) benzene waste operations (5,300 kkg/year), (3) gasoline marketing systems, including bulk gasoline terminals and plants, service stations, and delivery tank trucks (4,800 kkg/year), (4) transfer operations at chemical production facilities, bulk terminals, and coke by-product recovery plants (4,600 kkg/year), (5) benzene storage vessels (620-1,290 kkg/year), (6) industrial solvent use (450 kkg/year), (7) chemical manufacturing process vents (340 kkg/year), and (8) ethylbenzene/styrene process vents (135 kkg/year). The 1984 benzene emission inventory for



California totaled 19,350 metric tons/year (17,500 kkg/year), with motor vehicle exhaust accounting for 71% of the total emissions (Allen 1987). Benzene is present in passenger car tailpipe emissions at a composition ranging from 2.9% to 15% of the total tailpipe hydrocarbon composition (Black et al. 1980). The contribution of mobile source hazardous air pollutant emissions has been compared to that of stationary sources in the Seattle-Tacoma area. Mobile sources were estimated to contribute approximately 83% of the benzene from stationary area and mobile sources combined, with major stationary point sources excluded (Mangino and Jones 1994). Another source of atmospheric benzene is cigarette smoke and exhaled breath of smokers (Wallace 1989a, 1989b; Wallace and Pellizzari 1986; Wester et al. 1986). Other releases of benzene to the atmosphere include structural fires (Lowry et al. 1985) off-gassing from particle board (Glass et al. 1986), vaporization from oil spills, and emissions from landfills (Bennett 1987; HSDB 1996; Wood and Porter 1987). According to TRI, an estimated total of 10.2 million pounds of benzene, amounting to approximately 96.2% of the total environmental release, was discharged to air from manufacturing and processing facilities in the United States in 1993 (TRI93 1995). Table 5-1 lists the amounts released from these facilities. The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list.

There is a potential for atmospheric release of benzene from hazardous waste sites. Benzene has been detected in air in 136 of the 816 current and former NPL sites where benzene has been detected in some medium (HazDat 1996).

### 5.2.2 Water

Benzene is released to water from the discharges of both treated and untreated industrial waste water, leachate from landfills and other contaminated soils, gasoline leaks from underground storage tanks, and from accidental spills during marine transportation of chemical products (CDC 1994; Crawford et al. 1995; EPA 1979a; NESCAUM 1989; Staples et al. 1985). A fire in a tire dump site in western Frederick county, Virginia, produced a free-flowing oily tar containing benzene among other chemicals. The seepage from this site contaminated nearby surface water (EPA 1993j). Between 1986 and 1991, 3,000 gallons of benzene were accidentally released into Newark Bay and its major tributaries. Another 3,000 gallons were released in 1991 (Crawford et al. 1995). According to TRI, approximately 18,700 pounds of benzene, amounting to approximately 0.2% of the total environmental release, were discharged to water from manufacturing and processing facilities in the United States in

Table 5-1. Releases to the Environment from Facilities That Manufacture or Process Benzene

State <sup>b</sup>	Number of facilities	Range of reported amounts released in pounds per year <sup>a</sup>						
		Air	Water	Land	Underground injection	Total environment <sup>c</sup>	POTW transfer	Off-site waste transfer
AK	4	10-39505	0-9	0-250	0	10-39516	0-5	0-1588
AL	18	45-134800	0-250	0-2	0-13	45-134800	0-501	0-282935
AR	4	250-69879	0	0	0-5	255-69879	0	0-95600
AZ	2	94-260	0	0	0	94-260	0-2	0-229
CA	35	0-26000	0-630	0-250	0-197	0-26630	0-30000	0-2814
CO	2	4900-20075	0-1	0	0	4901-20075	0	0-175
DE	4	65-47996	0-550	0-100	0	65-48011	0	20-235
GA	6	0-32114	0-5	0-250	0	0-32115	0	0-12190
HI	2	17600-29100	0	0-5	0-5	17605-29105	0	0-10
IA	1	15700	0	0	0	15700	0	173
IL	26	44-246000	0-750	0-320	0	44-246000	0-2232	0-900000
IN	18	0-80411	0-250	0-1400	0-7000	0-80411	0-3700	0-25414
KS	10	89-47000	0-230	0-3084	0	89-47230	0-1833	0-4182
KY	12	15-185634	0-250	0-250	0	15-185702	0-70	0-801433
LA	40	1-178000	0-680	0-370	0-6700	1-178025	0	0-23157
MD	3	58-3400	0	0-675	0	58-4075	0-30	0-65560
MI	28	4-102693	0-30	0	0-9000	4-102693	0-11949	0-280363
MN	3	180-174500	0-13	0	0	180-174500	0	0-5
MO	7	3-770	0	0	0	3-770	0-250	0-840
MS	6	250-112000	0-250	0-250	0	500-112058	0-6	0-240
MT	4	3750-18900	0-5	0-76	0	3754-18910	0-5	5-48
NC	3	950-88427	0-1	0-1	0	950-88427	0	0-360
ND	1	44500	0	1	0	44501	0	49
NE	1	500	0	0	0	500	0	0
NJ	12	30-68300	0-2403	0-10	0	30-68300	0-75000	0-183000
NM	4	10-24758	0	0-500	0	10-25008	0	0-755
NY	5	5-4425	0-5	0-250	0	5-4430	0-250	0-6614
OH	25	5-188924	0-250	0-350	0-3	5-188924	0-124	0-11700

Table 5-1. Releases to the Environment from Facilities That Manufacture or Process Benzene (continued)

State <sup>b</sup>	Number of facilities	Range of reported amounts released in pounds per year <sup>a</sup>						
		Air	Water	Land	Underground injection	Total environment <sup>c</sup>	POTW transfer	Off-site waste transfer
OK	6	312-38100	0-46	0-250	0	312-38355	0	0-1334
OR	1	15003	0	0	0	15003	206	65
PA	21	100-170000	0-250	0-428	0	100-170130	0-65000	0-286081
PR	5	250-125696	0	0-1089	0	250-125696	0	0-29
SC	3	1600-262768	0-198	0	0	1600-262966	0	0-52038
TN	9	0-41900	0-5	0	0-1	0-41900	0-4631	0-32800
TX	94	1-372368	0-1520	0-2531	0-117517	5-372990	0-39664	0-633368
UT	8	1440-10222	0	0-100	0	1440-10222	0-11000	0-25
VA	5	44-302000	0-1360	0	0	44-302002	0-456	0-200
VI	1	86389	819	1454	0	88662	0	448
WA	6	8995-33400	0-10	0-250	0	9005-33655	0	0-255
WI	4	10-7441	0	0-334	0	10-7656	0	0-3700
WV	8	12-243000	0-310	0-250	0	12-243005	0	0-2534
WY	5	1290-8470	0-5	0-500	0	1290-8480	0	0-250

Source: TRI93 1995

<sup>a</sup> Data in TRI are maximum amounts released by each facility.<sup>b</sup> Post office state abbreviations used<sup>c</sup> The sum of all releases of the chemical to air, land, water, and underground injection wells by a given facility

POTW = publicly owned treatment works

1993 (TRI93 1995). Another 363,700 pounds were released to publicly owned waste water treatment plants (TRI93 1995). Although the major portion of benzene will biodegrade during the treatment processes, a small but undetermined portion will volatilize and a portion will remain unaltered. The ultimate discharge of the treated waste water will release benzene to natural bodies of water. Table 5-1 lists the amounts released from these facilities. The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list.

There is a potential for release of benzene to water from hazardous waste sites. Benzene has been detected in groundwater samples collected at 686 of the 816 current and former NPL sites, in surface water samples collected at 172 of the 816 sites, and in leachate samples collected at 112 of the 816 sites where benzene has been detected in some medium (HazDat 1996).

### 5.2.3 Soil

Benzene is released to soils through industrial discharges, land disposal of benzene-containing wastes, and gasoline leaks from underground storage tanks. In northern Virginia, approximately 200,000 gallons of liquid hydrocarbons were released from a fuel-storage terminal into the underlying soil (Mushrush et al. 1994). According to TRI, approximately 21,500 pounds of benzene were released to land from manufacturing and processing facilities in the United States in 1993 (TRI93 1995). An additional □364,000 pounds of benzene were released to soil by underground injection from manufacturing and processing facilities in the United States in 1993 (TRI93 1995). These combined releases amount to approximately 3.6% of the total environmental release. Table 5-1 lists the amounts released from these facilities. The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list.

There is a potential for release of benzene to soil from hazardous waste sites. Benzene has been detected in soil samples collected at 312 of the 816 current and former NPL sites, in soil gas samples collected at 69 of the 816 sites, and in sediment samples collected at 125 of the 816 sites where benzene has been detected in some medium (HazDat 1996).

### 5.3 ENVIRONMENTAL FATE

#### 5.3.1 Transport and Partitioning

The high volatility of benzene is the controlling physical property in the environmental transport and partitioning of this chemical. Benzene is considered to be highly volatile with a vapor pressure of 95.2 mm Hg at 25 °C. Benzene is slightly soluble in water, with a solubility of 1,780 mg/L at 25 °C, and the Henry's law constant for benzene ( $5.5 \times 10^{-3}$  atm-m<sup>3</sup>/mole at 20 °C) indicates that benzene partitions readily to the atmosphere from surface water (Mackay and Leinonen 1975). Mackay and Leinonen (1975) estimated a volatilization half-life for benzene of 4.81 hours for a 1-meter-deep body of water at 25 °C. Even though benzene is only slightly soluble in water, some minor removal from the atmosphere via wet deposition may occur. A substantial portion of any benzene in rainwater that is deposited to soil or water will be returned to the atmosphere via volatilization.

Benzene released to soil surfaces partitions to the atmosphere through volatilization, to surface water through runoff, and to groundwater as a result of leaching. A useful parameter for investigating the leachability of a chemical is the soil organic carbon sorption coefficient ( $K_{oc}$ ). According to Kenaga (1980), compounds with a  $K_{oc}$  of <100 are considered to be moderately to highly mobile. Benzene, with a  $K_{oc}$  value of 60-83 (Karickhoff 1981; Kenaga 1980), would be considered highly mobile. Other parameters that influence leaching potential include the soil type (e.g., sand versus clay), the amount of rainfall, the depth of the groundwater, and the extent of degradation. In a study of the sorptive characteristics of benzene to groundwater aquifer solids, benzene showed a tendency to adsorb to aquifer solids. Greater adsorption was observed with increasing organic matter content (Uchirin and Mangels 1987). An investigation of the mechanisms governing the rates of adsorption and desorption of benzene by dry soil grains revealed that periods of hours are required to achieve equilibrium and that adsorption is much faster than desorption (Lin et al. 1994). A model developed to predict the environmental fate of benzene following leakage of gasoline from an underground storage tank at Vero Beach in Florida indicated that most (67%) of the benzene in the gasoline would volatilize from this shallow sandy soil within 17 months. Of the remaining benzene, 29% would leach to groundwater, 3% would remain in the soil, and 1% would be degraded (Tucker et al. 1986). According to the model, the rate of volatilization and leaching would be the principal factors in determining the persistence of benzene in sandy soils.

The bioconcentration bioaccumulation potential of benzene in aquatic organisms of the open coastal ocean was investigated by sampling final effluent from the Los Angeles County waste water treatment plant quarterly from November 1980 to August 1981 (Gossett et al. 1983). The benzene concentration was 0.22 ppm. The results show that the bioconcentration is related to the *n*-octanol/water partition coefficient ( $K_{ow}$ ). Benzene has a relatively low partition coefficient ( $\log K_{ow} = 2.13$  or 2.15) (Gossett et al. 1983; HSDB 1996) and although its concentration in the effluent water was high, its bioaccumulation in fish liver was low (0.001-0.052  $\mu\text{g/g}$  wet weight). In the alga *Chlorella*, a bioaccumulation factor of 30 was determined experimentally and a bioconcentration factor of 40 was estimated from regression equation using a value of  $K_{ow}$  (Geyer et al. 1984). These findings suggest that bioaccumulation/bioconcentration in marine organisms is not significant and can be estimated by using the *n*-octanol/water partition coefficient. Similar results were reported by Miller et al. (1985) who used a log octanol-water partition coefficient of 2.13 and an estimated bioconcentration factor (BCF) of 24 to conclude that benzene is not expected to bioconcentrate to any great extent in aquatic organisms. An experimental BCF of 4.27 was measured in goldfish reared in water containing 1 ppm of benzene (Ogata et al. 1984). Based on these estimated and measured values, bioconcentration/bioaccumulation of benzene in the aquatic food chains does not appear to be important. There is no evidence in the literature of biomagnification of benzene in aquatic food chain (e.g., increased accumulation from algae to algae-eating fish).

Evidence exists for the uptake of benzene by cress and barley plants from soil (Scheunert et al. 1985; Topp et al. 1989). BCFs for barley plants after 12, 33, 71, and 125 days were 17, 2.3, 2.9, and 4.6, respectively. BCFs for cress plants after 12, 33, and 79 days were 10, 2.3, and 1.9, respectively. The relative decrease in the BCFs with time was attributed to growth dilution (Topp et al. 1989). However, since benzene exists primarily in the vapor phase, air-to-leaf transfer rather than root uptake is considered to be the major pathway of vegetative contamination (Hattemer-Frey et al. 1990). Based on an equation to estimate vegetative contamination, the total concentration of benzene on exposed food crops consumed by humans and used as forage by animals was estimated to be 587 ng/kg, 81% of which was from air-to-leaf transfer and 19% from root uptake (Hattemer-Frey et al. 1990).

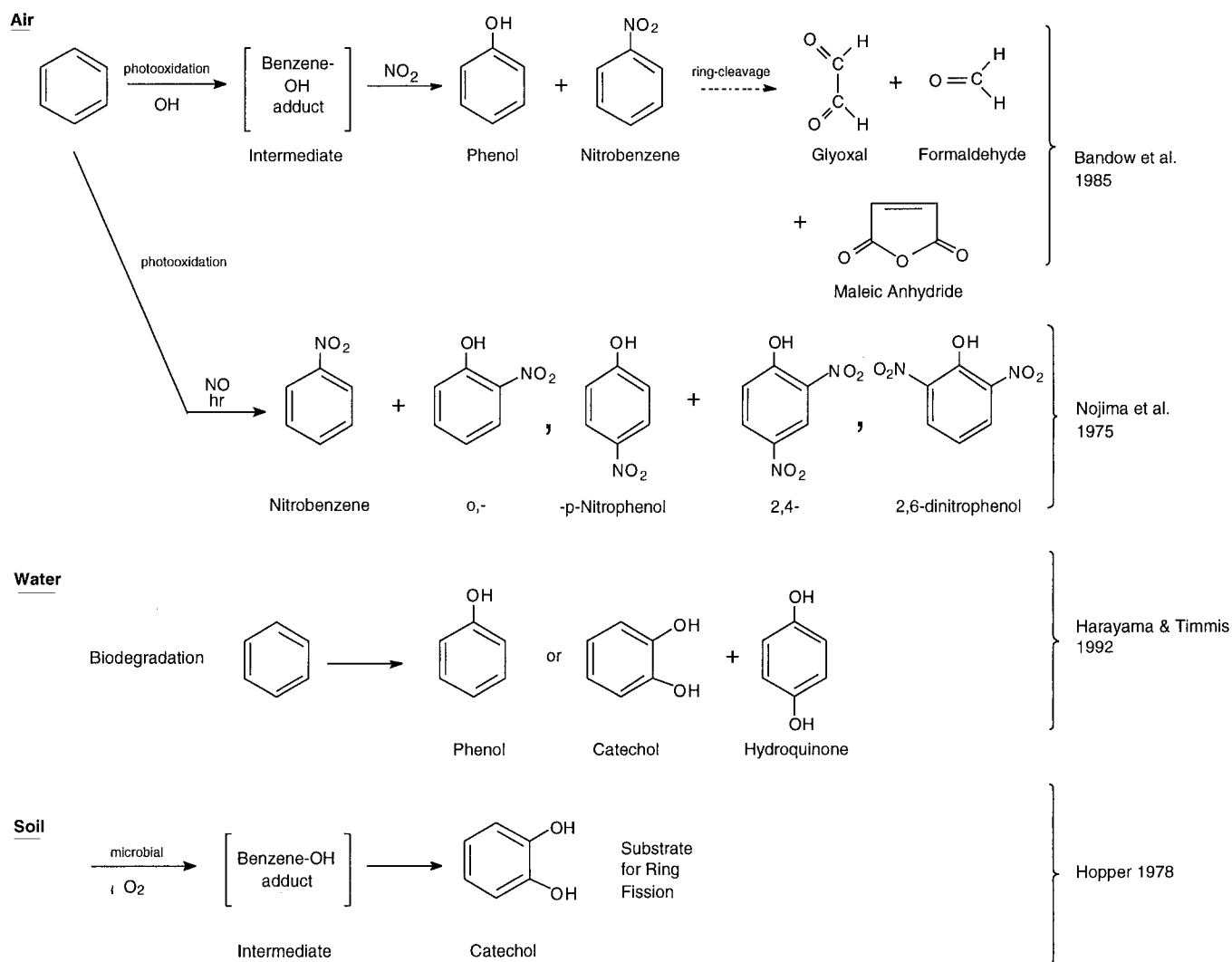
### 5.3.2 Transformation and Degradation

Benzene undergoes a number of different transformation and degradation reactions in the environment as discussed in the following sections. The resulting environmental transformation products within different media are shown in Figure 5-2.

#### 5.3.2.1 Air

Benzene in the atmosphere exists predominantly in the vapor phase (Eisenreich et al. 1981). The most significant degradation process for benzene is its reaction with atmospheric hydroxyl radicals. The rate constant for the vapor phase reaction of benzene with photochemically produced hydroxyl radicals has been determined to be  $1.3 \times 10^{-2} \text{ cm}^3/\text{molecule-second}$ , which corresponds to a residence time of 8 days at an atmospheric hydroxyl radical concentration of  $1.1 \times 10^6 \text{ molecules/cm}^3$  (Gaffney and Levine 1979; Lyman 1982). With a hydroxyl radical concentration of  $1 \times 10^8 \text{ molecules/cm}^3$ , corresponding to a polluted atmosphere, the estimated residence time is shortened to 2.1 hours (Lyman 1982). Residence times of 472 years for rural atmospheres and 152 years for urban atmospheres were calculated for the reaction of benzene with ozone ( $\text{O}_3$ ) using a rate constant for  $\text{O}_3$ , of  $7 \times 10^{-23} \text{ cm}^3/\text{molecule-second}$  (Pate et al. 1976) and atmospheric concentrations for  $\text{O}_3$  of  $9.6 \times 10^{11} \text{ molecules/cm}^3$  (rural) and  $3 \times 10^{12} \text{ molecules/cm}^3$  (urban) (Lyman 1982).

The reaction of benzene and nitric oxide in a smog chamber was investigated to determine the role of benzene in photochemical smog formation (Levy 1973). The results showed that benzene exhibited low photochemical smog reactivity in the four categories tested: rate of photooxidation of nitric oxide, maximum oxidant produced, eye-irritation response time, and formaldehyde formation. The authors concluded that benzene probably does not play a significant role in photochemical smog formation (Levy 1973). However, data show that, in the presence of active species such as nitrogen oxides and sulfur dioxide, the rate of photodegradation of benzene in the gas phase was greater than that in air alone. Its half-life in the presence of such active species (100 ppm benzene in the presence of 10-110 ppm  $\text{NO}_x$  or 10-100 ppm  $\text{SO}_2$ ) was 4-6 hours with 50% mineralization to carbon dioxide in approximately 2 days (Korte and Klein 1982). Some of the products of the reaction of benzene with nitrogen monoxide gas (e.g., nitrobenzene, *o*- and *p*-nitrophenol, and 2,4- and 2,6-dinitrophenol) may have potentially adverse effects on human health (Nojima et al. 1975). Photooxidation of benzene in a

**Figure 5-2. Environmental Transformation Products of Benzene in Various Media**

nitrogen monoxide/nitrogen dioxide-air system formed formaldehyde, formic acid, maleic anhydride, phenol, nitrobenzene, and glyoxal (Bandow et al. 1985).

Direct photolysis of benzene in the atmosphere is not likely because the upper atmosphere effectively filters out wavelengths of light less than 290 nm, and benzene does not absorb wavelengths of light greater than 260 nm (Bryce-Smith and Gilbert 1976).

#### 5.3.2.2 Water

McAllister and Chiang (1994) have summarized the natural attenuation of benzene, toluene, ethylbenzene, and *o*-, *m*-, and *p*-xylene (BTEX) in groundwater. They report that aerobic biodegradation is expected to be the primary mechanism for degradation of BTEX. Dispersion will reduce the concentration of benzene (or any contaminant) as the contaminated water migrates from the source. Volatilization is expected to account for approximately 5-10% of natural attenuation at most sites (McAllister and Chiang 1994). Sensitivity testing of groundwater models with subsurface characteristics and monitoring well data have shown that 80-100% of BTEX in plumes must have been removed by biotransformation processes within 1-1.5 years. The main factor limiting biodegradation was the dissolved oxygen concentration in the groundwater (Salanitro 1993).

A half-life of 16.9 days was reported for photolysis of benzene dissolved in oxygen-saturated deionized water and exposed to sunlight (Hustert et al. 1981). For reaction with hydroxyl radicals, an estimated half-life of 0.71 years has been calculated, which is much slower than the same reaction in air (Anbar and Neta 1967).

Benzene is biodegradable in surface water and groundwater. Microbial degradation of benzene in aquatic environments is influenced by many factors such as microbial population, dissolved oxygen, nutrients, other sources of carbon, inhibitors, temperature, and pH. One study reported biodegradation half-lives for benzene in surface water (river water) and groundwater of 16 and 28 days, respectively. Benzene was found to be resistant to biodegradation in surface water taken from a harbor and supplemented with either nutrients (nitrogen and phosphorus) or acclimated microbes. Biodegradation did occur, with a half-life of 8 days, in surface water enriched with both nutrients and microbes (Vaishnav and Babeu 1987). In another study, Davis et al. (1994) observed rapid aerobic biodegradation of benzene in aquifer groundwater samples and measured times for 50% disappearance

ranging from 4 days for an initial benzene concentration of  $\approx 1$  mg/kg to 14 days for an initial benzene concentration of  $\approx 10$  mg/kg.

Under aerobic conditions (pH 5.3, 20 °C), benzene was completely microbially degraded in 16 days in groundwater taken from a shallow well (Delfino and Miles 1985). The aerobic biodegradation of benzene is also influenced by the presence of other aromatic hydrocarbons. A bacterial culture grown with aromatic hydrocarbons plus nitrogen-, sulfur-, and oxygen-containing aromatic compounds was much less efficient in degrading benzene than the culture grown with aromatic hydrocarbons alone. Pyrrole strongly inhibited benzene degradation. Benzene degradation was high when toluene and xylene were present (Arvin et al. 1989).

An analysis of benzene, toluene, and xylene (BTX) in groundwater from a field site indicated that the amount of BTX in groundwater was inversely related to the availability of dissolved oxygen (Chiang et al. 1989). Results of biodegradation experiments in laboratory microcosms using groundwater from the field site showed the following results at BTX levels of 120-16,000 ppb: BTX degradation was 80-100% (half-life of 5-20 days) when the dissolved oxygen level was  $\geq 2$  ppm; BTX degradation was slowed (half-life of 20-60 days) when the dissolved oxygen level was  $< 2$  ppm; and little or no degradation of BTX occurred when the dissolved oxygen level was 0, 0.1, or 0.5 ppm (Chiang et al. 1989).

Several pure cultures of microorganisms isolated from water including several *Pseudomonas* sp. (Chang et al. 1993; Harayama and Timmis 1992), *Mycobacterium vaccae* (Burbach and Perry 1993), and a strain of *Pseudomonas fluorescens* (Mikesell et al. 1993), can catabolize benzene in water under aerobic conditions. A strain of *P. fluorescens* can catabolize benzene under oxygen-limiting conditions (initial dissolved oxygen concentration of about 2 mg/L) with nitrate as alternate electron acceptor (Mikesell et al. 1993; Olsen et al. 1994). If the bacteria contain ring-hydroxylating monooxygenases (e.g., *P. fluorescens*) they catabolize benzene to phenol; while ring dioxygenases (e.g., *P. urviella*) catabolize benzene to pyrocatechol and hydroquinone (Harayama and Timmis 1992). Ring cleavage by dioxygenases requires aromatic compounds carrying two hydroxyl groups, one in the ortho or para position (Harayama and Timmis 1992).

Laboratory studies on microbial degradation of benzene with mixed cultures of microorganisms in gasoline-contaminated groundwater revealed that both oxygen and nitrogen concentrations are major

controlling factors in the biodegradation of benzene. A natural mix of adapted microorganisms, obtained by selective enrichment, was used as the inoculum to accelerate the biochemical breakdown of benzene in groundwater. The inoculum plus nitrogen amendments enhanced the biodegradation rate of benzene 4.5-fold at 23 °C using a shaker flask system. More than 95% of the benzene in groundwater was removed through microbial action within 73.5 hours (Karlson and Frankenberger 1989). Similarly, a mixed culture consortia obtained from subsurface sediments degraded 1 mg/L benzene in water at an initial rate of 167 µg/L/day to below detectable limits (detection limit not given) by a continuously recycled bioreactor within 8-10 days (Korde et al. 1993). Results of a biochemical oxygen demand (BOD) test determined that benzene was completely biodegradable after the second week of static incubation at 25 °C at benzene concentrations of 5 and 10 mg/L using domestic waste water as the microbial inoculum (Tabak et al. 1981). A study of the degradation of benzene by the microbial population of industrial waste water at 23 °C using a shaker flask system showed that after 6 hours, only 4 mg/L of benzene remained of the 50 mg/L dose (Davies et al. 1981). Produced water from a petroleum production site has been successfully biotreated for complete removal of benzene using a flocculated culture of *T. denitrificans* strain F and mixed heterotrophs (Rajganesht et al. 1995).

When dissolved oxygen is depleted, an alternative electron acceptor such as nitrate, carbonate, or iron(III) must be available, and microbes capable of using the alternative electron acceptor to degrade the benzene must be present (McAllister and Chiang 1994). Benzene biodegradation under anaerobic conditions is much slower than under aerobic conditions. No significant benzene biodegradation was reported during the first 20 weeks of incubation under anaerobic conditions at 17 °C; however, after 40 weeks of incubation, benzene concentrations were reduced by 72% (Wilson et al. 1986). After 120 weeks of incubation, over 99% degradation had taken place (Wilson et al. 1986). No degradation of benzene was observed in 96 days under anaerobic conditions (20 °C) using raw water intake from a water treatment plant (Delfino and Miles 1985). Use of water as an oxygen source in the anaerobic degradation of benzene has been demonstrated. Experiments indicated that incorporation of <sup>18</sup>O from <sup>18</sup>O-labeled water is the initial step in the anaerobic oxidation of benzene by acclimated-methanogenic cultures. Phenol was the first major product (Vogel and Grbić-Galić 1986). BTX was degraded under denitrifying conditions in anaerobic batch microcosms (10 °C) containing shallow aquifer material. BTX loss was greater with the addition of nitrate. Some degradation occurred without the addition of nitrogen or oxygen (Major et al. 1988).

### 5.3.2.3 Sediment and Soil

Benzene is biodegraded in soil under aerobic conditions. Microbial metabolism of benzene proceeds through the formation of *cis*-dihydrodiols and, with further metabolism, to catechols, which are the substrates for ring fission (Gibson 1980; Hopper 1978). *Pseudomonas putida* oxidized benzene through *cis*-1,2-dihydroxy-1,2-dihydrobenzene (Gibson 1977; Hopper 1978). *Norcardia* species and *Pseudomonas* species, after acclimation, effectively degraded benzene to carbon dioxide after 7 days (45-90%). A strain of *Rhodococcus* isolated from a contaminated river sediment mineralized 71% of benzene at an initial concentration of 0.7 mg/L in 14 days (Malachowsky et al. 1994). The soil bacterium *Nitrosomonas europaea* catabolized benzene to phenol and hydroquinone (Keener and Arp 1994a). A strain of *Pseudomonas putida* developed by encoding of genes completely mineralized benzene (Lee et al. 1994). Another new mixotrophic bacteria, a strain of *Pseudomonas sp.* isolated from contaminated soil, grew under both anaerobic and aerobic conditions and used benzene for its growth (Morikawa and Imanaka 1993).

Salanitro (1993) has summarized the aerobic degradation rates for BTEX in laboratory subsoilgroundwater slurries and aquifers. The data indicate that decay rates for benzene are highest (19-52% per day) for benzene concentrations less than 1 ppm when initial dissolved oxygen levels are about 8 ppm. Rates are significantly reduced (0-1.1% per day) when benzene levels are 1-2 ppm, and no degradation was observed when benzene levels were greater than 2 ppb.

*In situ* microcosms (ISM) and laboratory batch microcosms (LBM) have been used to determine the first-order degradation rate constants of benzene in an aerobic aquifer (Nielsen et al. 1996). Degradation rate constants for benzene for three ISMs ranged from 0.2 to 0.5 day<sup>-1</sup> with lag times of 1-6 days. In the 3 corresponding LBMs, the degradation rate constants ranged from 0.07 to 0.2 day<sup>-1</sup> with lag times of 0-5 days. The first-order degradation rate constants measured in this study are much lower than the rate constant of 18 day<sup>-1</sup> obtained from column experiments in another study (Anglely et al. 1992).

Benzene has been shown to be anaerobically transformed by mixed methanogenic cultures derived from ferulic acid-degrading sewage sludge enrichments. In most of the experiments, toluene or benzene were the only semicontinuously supplied energy sources in the defined mineral medium (Grbic-Galic and Vogel 1987). At least 50% of the substrates were converted to CO<sub>2</sub> and methane.

An initial lag time of 11 days occurred before the onset of gas production with 15 mM benzene. The intermediates were consistent with benzene degradation via initial oxidation by ring hydroxylation.

It has been demonstrated that when mixtures of benzene, toluene, xylenes, and ethylbenzene are present in an anaerobic environment, there is a sequential utilization of the substrate hydrocarbons, with toluene usually being the first to be degraded, followed by the isomers of xylene in varying order. Benzene and ethylbenzene tend to be degraded last if they are degraded at all (Edwards and Grbic-Galic 1992). To test the hypothesis that benzene degradation was prevented by the presence of other more suitable substrates, a study was carried out using sediment microcosms amended with benzene only. Benzene at initial concentrations ranging from 40 to 200  $\mu\text{M}$  was depleted in all microcosms, with degradation rates ranging from 0.36 to 3.7  $\mu\text{M}/\text{day}$  depending upon substrate concentration and the presence of other carbon sources (Edwards and Grbic-Galic 1992).

The biodegradation of 2 mg of radiolabeled benzene in 100 g of soil with a mixed microbial population transformed only 47% of the added radioactivity to carbon dioxide after 10 weeks (Haider et al. 1981). The authors concluded that specific organisms that mineralize benzene were present in the soil in only small numbers. ULTRA, a fate and transport model used to predict the environmental fate of benzene following leakage of gasoline from an underground storage tank into shallow sandy soil, indicated that only about 1% of the benzene in the gasoline would be degraded over a 17-month period, and 3% would remain in the soil (Tucker et al. 1986). Of the benzene that leaked in soil, the highest percentages would either volatilize (67%) or get into groundwater (29%) according to this model.

#### **5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT**

Reliable evaluation of the potential for human exposure to benzene depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. In reviewing data on benzene levels monitored in the environment, it should also be noted that the amount of-chemical identified analytically is not necessarily equivalent to the amount that is bioavailable.

#### 5.4.1 Air

Benzene is ubiquitous in the atmosphere. It has been identified in outdoor air samples of both rural and urban environments and in indoor air. Table 5-2 lists benzene levels in outdoor air from various cities in the United States.

Volatile organic compounds, including benzene, were measured at 11 monitoring sites in Anchorage, Alaska, in a year-long study ending in April 1994 (Taylor and Morris 1995). The study was initiated in response to concerns by residents about petroleum odors from several large fuel storage facilities located just north and west of an Anchorage neighborhood. Average annual benzene concentrations ranged from a minimum of 1.15 parts per billion by volume (ppbv) in a low density residential area to 5.44 ppbv near a major midtown intersection. In the neighborhood where residents were complaining of petroleum odors, the highest benzene concentrations (annual average 3.74 ppbv) were measured on a cliff over the petroleum tank farm, within 50 meters of a petroleum storage tank. This site also showed peak benzene concentrations in summer, indicating warm weather evaporative emissions, while those in other areas showed peaks in winter, suggesting mobile sources as the main contributors.

Ambient air samples from 44 sites in 39 U.S. urban areas were collected from 6 a.m. to 9 a.m. during June through September of 1984, 1985, and 1986. Benzene was present in every sample. The median benzene site concentrations ranged from 4.8 to 35 ppb, with the overall median being 12.6 ppb (detection limit = 0.04 ppb). The data indicated that mobile sources were the major source of benzene in the vast majority of samples (EPA 1987e). In California, motor vehicle exhaust and motor vehicle evaporation accounted for 79.8% of the population exposure to ambient benzene (Allen 1987). The 1984 population-weighted average benzene concentration in California was estimated to be 3.3 ppb (Allen 1987).

The following daily median benzene air concentrations were reported by the Volatile Organic Compound National Ambient Database (1975-1985): remote (0.16 ppb), rural (0.47 ppb), suburban (1.8 ppb), urban (1.8 ppb), indoor air (1.8 ppb), and workplace air (2.1 ppb). The outdoor air data represent 300 cities in 42 states. The indoor air data represent 30 cities in 16 states (Shah and Singh 1988).

## 5. POTENTIAL FOR HUMAN EXPOSURE

**Table 5-2. Benzene Levels in Air Samples**

Location	Concentration (ppb)	Comments	References
<b>Outdoor air</b>			
San Francisco, CA	0.8–5.2 (range); 2.6 ± 1.3 <sup>a</sup>	Data from six different urban locations in 1984; N = 25	Wester et al. 1986
Stinson Beach, CA	0.38 ± 0.39 <sup>a</sup>	Data from remote coastal area in 1984; N = 21	Wester et al. 1986
Houston, TX	7.5–112.3 (range); 22.5 <sup>b</sup>	EPA survey, urban area; N = 14; summer 1986	EPA 1987e
Houston, TX	0.55–6.3; 1.73 <sup>b</sup>	Semirural area; N = 22; 1990–1991	Kelly et al. 1993
St. Louis, MI	3.8–72.7 (range); 11.1 <sup>b</sup>	EPA survey, urban area; N = 18; summer 1985	EPA 1987g
Denver, CO	17.9–39.5 (range); 24.5 <sup>b</sup>	EPA survey, urban area; N = 13; summer 1986	EPA 1987g
Philadelphia, PA	1.9–17.9 (range); 6.0 <sup>b</sup>	EPA survey, urban area; N = 14; summer 1985	EPA 1987g
New York (Manhattan), NY	5.3–31.8 (range); 10.5 <sup>b</sup>	EPA survey, urban area; N = 12; summer 1986	EPA 1987g
Chicago, IL	3.8–30.3 (range); 20.7 <sup>b</sup>	EPA survey, urban area; N = 14; summer 1986	EPA 1987g
Boston, MA	0.69–3.1; 1.06 <sup>b</sup>	Urban area; N = 22; 1990–1991	Kelly et al. 1993
New York (Staten Island), NY	0.1–34 (range); 4.4 ± 6.6 <sup>a</sup>	Urban area; spring 1984	Singh et al. 1985
73 km northwest of Denver, CO	0.02–0.85 (range)	Rural area; May 1981–Dec. 1982	Roberts et al. 1985
Elizabeth and Bayonne, NJ	Night 2.7 <sup>c</sup> , 28.5 (max); day, 3.0 <sup>c</sup> , 13.8 (max)	Night, N = 81–86; day, N = 86–90; fall 1981	Wallace et al. 1985
<b>Personal air</b>			
Elizabeth and Bayonne, NJ	Night 9.7 <sup>c</sup> , 159.6 (max); day, 8.5 <sup>c</sup> , 84.5 (max)	Night, N = 346–348; day, N = 339–341; fall 1981	Wallace et al. 1985

<sup>a</sup>Average ± standard deviation<sup>b</sup>Median<sup>c</sup>Weighted average

EPA = Environmental Protection Agency; max = maximum; N = number of samples

Analysis of ambient air samples collected in industrial areas showed benzene levels ranging from 0.4 to 16  $\mu\text{g}/\text{m}^3$  (0.13-5 ppb) in Iberville Parish, Louisiana, an area that included many organic chemical and petroleum producer, user, and storage facilities located along the Mississippi River (Pellizzari 1982). Indoor and outdoor air measurements were made in August 1987 in the Kanawha Valley region of West Virginia, which is the center of a heavily industrialized area known for its chemical manufacturing. The mean, maximum, and median indoor concentrations of benzene were 2.1, 14.9, and 0.64 ppb, respectively. The median outdoor ambient air concentration of benzene was 0.78 ppb (Cohen et al. 1989).

Concentrations of volatile organic compounds were measured in 12 northern California office buildings with three different types of ventilation. Benzene concentrations ranged from ~0.1 to 2.7 ppb, with a geometric mean of 0.98 ppb (Daisey et al. 1994).

Population-weighted personal exposures to benzene exceeded the outdoor air concentrations in data from EPA's Total Exposure Assessment Methodology (TEAM) study. The overall mean personal exposure was about 15  $\mu\text{g}/\text{m}^3$  (4.7 ppb), compared to an overall mean outdoor concentration of only 6  $\mu\text{g}/\text{m}^3$  (1.9 ppb) (Wallace 1989a). The study also reported that the median level of benzene in 185 homes without smokers was 7  $\mu\text{g}/\text{m}^3$  (2.2 ppb), and the median level of benzene in 343 homes with one or more smokers was 10.5  $\mu\text{g}/\text{m}^3$  (3.3 ppb) (Wallace 1989a). This finding points to the possible significance of passive smoking as a source of benzene exposure. Indoor air samples taken from a smoke-filled bar contained 8.1-11.3 ppb of benzene (Brunnemann et al. 1989). A study conducted by R.J. Reynolds Tobacco Company in smoking and nonsmoking homes revealed that benzene levels were elevated in smoking homes. In 24 nonsmoking homes, the mean benzene concentration was 3.86  $\mu\text{g}/\text{m}^3$  with a maximum of 18.96  $\mu\text{g}/\text{m}^3$ . In 25 smoking homes, the mean benzene concentration was 5.54  $\mu\text{g}/\text{m}^3$ , with a maximum of 26.96  $\mu\text{g}/\text{m}^3$ . However, benzene was not significantly correlated or associated with 3-ethenylpyridine, a proposed vapor phase environmental tobacco smoke marker (Heavner et al. 1995).

An analysis of landfill gas from 20 Class II (municipal) landfills revealed a maximum concentration of 32 ppm for benzene (Wood and Porter 1987). Benzene was measured in the vicinity of the BKK landfill, a hazardous waste landfill in California, at a maximum concentration of 3.8  $\mu\text{g}/\text{m}^3$  (1.2 ppb) (Bennett 1987). Maximum estimated levels of benzene in air near uncontrolled (Superfund) hazardous

waste sites were 190  $\mu\text{g}/\text{m}^3$  (59.5 ppb) at the Kin-But Landfill (Edison, New Jersey) and 520  $\mu\text{g}/\text{m}^3$  (162.8 ppb) in Love Canal basements (Niagara Falls, New York) (Bennett 1987; Pellizzari 1982).

#### 5.4.2 Water

Measured benzene levels in open ocean samples in the Gulf of Mexico in 1977 in relatively unpolluted waters ranged from 5 to 15 ng/kg (5-15 parts per trillion [ppt]); levels in polluted waters of the open ocean ranged from 5 to 40 ng/kg (5-40 ppt) (Sauer 1981). Benzene levels measured in coastal surface waters of the Gulf of Mexico were 6 ng/kg (6 ppt) in relatively unpolluted waters and 50-175 ng/kg (50-175 ppt) in polluted coastal waters (Sauer 1981). Benzene has been detected in rainwater in the United Kingdom at a concentration of 87.2 ppb (Colenutt and Thorburn 1980).

Data from EPA's STORage and RETrieval (STORET) database (1980-82) showed that benzene was positively detected in 15% of the surface water samples collected at 1,271 observation stations at a median concentration of 5 ppb. The sampling sites in the STORET database include both ambient and pipe sites. Ambient sites include streams, lakes, ponds, wells, reservoirs, canals, estuaries, and oceans and are intended to be indicative of general U.S. waterway conditions. Pipe sites refer to municipal or industrial influents or effluents (Staples et al. 1985).

Benzene levels in water in the vicinity of five industrial facilities using or producing benzene ranged from <1 ppb to a high of 179 ppb. The highest level (179 ppb) was found in plant effluent. In general, benzene in plant effluents quickly dispersed in rivers or streams to levels of 1-2 ppb or less (EPA 1979a). The maximum benzene levels observed in monitoring wells in plumes from fuel spills at gasoline service stations ranged from 1,200 to 19,000 ppb (Salanitro 1993). A monitoring well in the vicinity of a bulk storage facility had a maximum benzene level of 45,000 ppb (Salanitro 1993). In northern Virginia, approximately 200,000 gallons of liquid hydrocarbons were released from a fuel-storage terminal into the underlying soil. A dichloromethane extract of groundwater from a monitoring well in the same area gave a benzene concentration of 52.1 ppm (Mushrush et al. 1994). Benzene has been detected at concentrations ranging from 16 to 110 ppb in landfill leachate from a landfill that accepted both municipal and industrial wastes (Cline and Viste 1985).

Composite data from the Comprehensive Emergency Response, Compensation, and Liability Act (CERCLA) monitoring program indicate that benzene was detected at a frequency of 11.2% in

groundwater in the vicinity of 178 inactive hazardous waste disposal sites (Plumb 1987). Data from a 1980 national survey by the Council on Environmental Quality on groundwater and surface water contamination showed benzene concentrations in contaminated drinking water wells in New York, New Jersey, and Connecticut ranged from 30 to 330 ppb, with the highest concentration in drinking water from surface water sources reported to be 4.4 ppb (Burmaster 1982). Benzene has also been identified but not quantified as one of the major organic constituents in commercially bottled artisan water in the United States (Dowty et al. 1975). A survey of 182 samples of bottled drinking water, which consisted of 86 packaged (transparent plastic or glass) spring waters, 61 packaged (transparent plastic or glass) mineral waters, and 35 miscellaneous bottled waters, was conducted in Canada in 1990 (Page et al. 1993). At detection limits ranging from 0.2 to 1.0 ppb, benzene from unknown source(s) was detected in only one sample of bottled spring water at a concentration of 2 ppb.

#### **5.4.3 Sediment and Soil**

Benzene levels ranging from <2 to 191 ppb were recorded in the vicinity of five industrial facilities using or producing benzene (EPA 1979a). Sediment levels ranging from 8 to 21 ppb were detected in Lake Pontchartrain in Louisiana (Ferrario et al. 1985). In northern Virginia, approximately 200,000 gallons of liquid hydrocarbons were released from a fuel-storage terminal into the underlying soil. Soil gases measured at a depth of 10 feet about 1,000 feet from the storage terminal had a benzene concentration of 1,500 ppm (Mushrush et al. 1994). Data from EPA's STORET database (1980-1982) showed that benzene had been positively detected in sediment samples taken at 9% of 355 observation stations with a median level of <5 ppb (Staples et al. 1985). The concentration of benzene in soil near factories where benzene was produced or used ranged from 2 to 191 ppb (IARC 1982a).

#### **5.4.4 Other Environmental Media**

Benzene was detected in oysters and clams at levels of 220 and 260 ppb (wet weight), respectively, from Lake Pontchartrain in Louisiana in 1980 (Ferrario et al. 1985). Data on the occurrence of benzene in food are limited. Benzene has been reported to occur in fruits, fish, vegetables, nuts, dairy products, beverages, and eggs (EPA 1982e). Although benzene has been detected in dairy products, there is no evidence of the presence of benzene in either cow's milk or human breast milk (Hattermer-Frey et al. 1990). In many foods, including dairy products where benzene has been detected, the

presence of benzene is likely to be due to uptake from the air (Grob et al. 1990). This conclusion was supported by the facts that the uptake decreased with decrease in exposed surface area of foods and contact time with air (Grob et al. 1990). Only a small number of these foods have been analyzed quantitatively. Eggs had the highest concentrations (2,100 ppb [uncooked] and 500-1,900 ppb [hard-boiled]), followed by haddock (100-200 ppb), Jamaican rum (120 ppb), irradiated beef (19 ppb), heat-treated canned beef (2 ppb), and butter (0.5 ppb). Lamb, mutton, veal, and chicken all had <10 ppb benzene (when the meats were cooked) (EPA 1980b, 1982e). A more recent survey of more than 50 foods collected and analyzed from 1991 to early 1992 (McNeal et al. 1993) revealed that foods (including eggs without added benzoates contained benzene at levels  $\leq 2$  ng/g. The level of benzene ) in foods containing added benzoates in addition to ascorbates (for example, imitation strawberry preserves, taco sauce, and duck sauce) ranged from <1 to 38 ng/g.

As part of a program to identify possible exposures that may be important in the high incidence of lung cancer among women in Shanghai, Pellizzari et al. (1995) qualitatively identified the volatile components emitted during heating of cooking oils to 265 °C. This study found that, on a relative basis, the intensity of the benzene peak in the total ion current chromatogram of vapors from Chinese rapeseed oil (commonly used in wok cooking) was 14-, 6.6-, and 1.7-fold greater than in vapors from peanut, soybean, and other canola (rapeseed) oils, respectively.

The amount of benzene measured in mainstream smoke ranged from 5.9 to 73  $\mu\text{g}/\text{cigarette}$  (Brunnemann et al. 1990). Larger amounts of benzene were found in sidestream smoke, ranging from 345 to 653  $\mu\text{g}/\text{cigarette}$  (Brunnemann et al. 1990).

## 5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

The Total Exposure Assessment Monitoring (TEAM) studies, carried out by the EPA between 1980 and 1990, suggested that for many chemicals, including benzene, the most important sources of pollution are small and close to the person, and that exposures are not clearly correlated-with emissions. For example, the TEAM study findings indicated that, although nearly 85% of atmospheric benzene in outdoor air is produced by cars burning petroleum products and the remaining 15% is produced by industry, about half of the total national exposure to benzene comes from cigarette smoke (Wallace 1995). In fact, breath measurements of benzene provided by the TEAM study between 1979 and 1988 identified smoking as the single most important source of benzene exposure for about

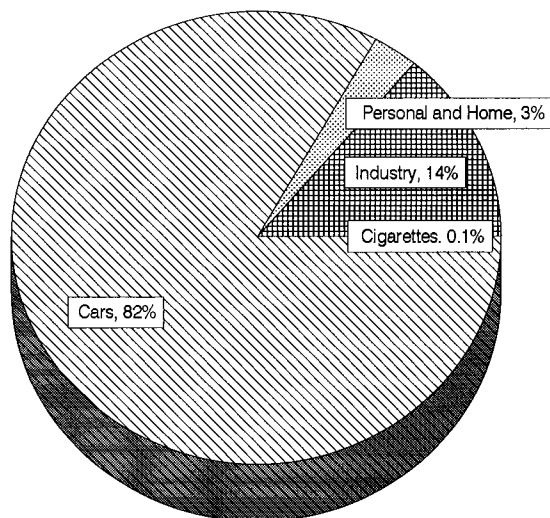
40 million U.S. smokers (Wallace 1989b). Even passive exposure to cigarette smoke is responsible for more benzene exposure (about 5% of the total) than the emissions from the entire industrial capacity of the United States (about 3% of the total) (Wallace 1995). A breakdown of the emissions and exposure sources for benzene that was derived from the Los Angeles TEAM study data (Wallace et al. 1991) is given in Figure 5-3. The reason that a relatively small source of emissions can have such a large effect on exposure is the efficiency of delivery. Wallace (1995) reports that one cigarette delivers an average of 55  $\mu\text{g}$  of benzene with nearly 100% efficiency to the smoker. Benzene from industrial sources is dissipated into the atmosphere.

Smokers ( $n=200$ ) in the TEAM study had a mean breath concentration of 15  $\mu\text{g}/\text{m}^3$  (4.7 ppb), almost 10 times the level of 1.5-2  $\mu\text{g}/\text{m}^3$  (0.47-0.63 ppb) observed in more than 300 non-smokers (Wallace 1989b). Smokers also had about 6-10 times as much benzene in their blood as non-smokers (Wallace 1995). In another study, benzene concentrations were compared in the breath of smokers and nonsmokers and in ambient air in both an urban area of San Francisco and in a more remote area of Stinson Beach, California (Wester et al. 1986). In the urban area, benzene in smokers' breath ( $6.8 \pm 3.0$  ppb) was greater than in nonsmokers' breath ( $2.5 \pm 0.8$  ppb) and smokers' ambient air ( $3.3 \pm 0.8$  ppb). In the remote area, the same pattern was observed: benzene in smokers' breath ( $12.1 \pm 9.6$  ppb) was higher than in nonsmokers' breath ( $1.8 \pm 0.2$  ppb) and ambient air ( $1.0 \pm 0.1$  ppb). Benzene in the nonsmokers' breath ( $2.5 \pm 0.8$  ppb) in the urban area was greater than in the nonsmokers' breath ( $1.8 \pm 0.2$  ppb) in the remote area. The results also showed that, in the urban area, benzene in the breath of nonsmokers ( $2.5 \pm 0.8$  ppb) was greater than in nonsmokers' ambient air ( $1.4 \pm 0.1$  ppb). The same was true in the remote area, where benzene in nonsmokers' breath ( $1.8 \pm 0.2$  ppb) was greater than in ambient air ( $1.0 \pm 0.1$  ppb). This suggests an additional source of benzene other than outdoor ambient air (Wester et al. 1986). In 10 of 11 homes inhabited by tobacco smokers, mean indoor and personal benzene concentrations were 2-5 times higher than outdoor levels (Thomas et al. 1993).

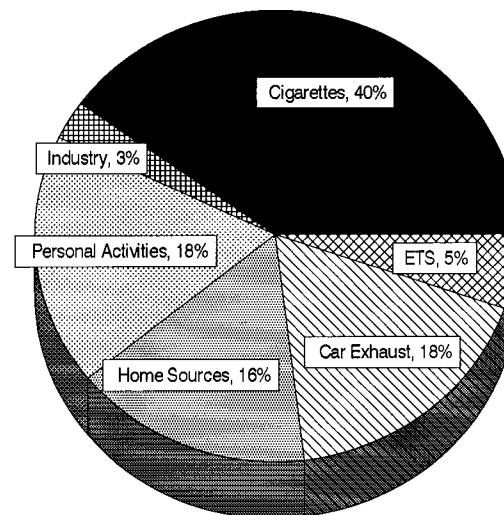
Assuming that the average sales-weighted tar and nicotine cigarette yields 57  $\mu\text{g}$  benzene in mainstream smoke, Wallace (1989a) estimates that the average smoker (32 cigarettes per day) takes in about 1.8 mg benzene per day from smoking. This is nearly 10 times the average daily intake of nonsmokers (Wallace 1989a). On the assumption that intake of benzene from each cigarette is 30  $\mu\text{g}$ , Fishbein (1992) has calculated that a smoker who consumes 2 packs of cigarettes per day will have an additional daily intake of 1,200  $\mu\text{g}$ .

**Figure 5-3. Benzene Emissions and Exposures**

## Benzene Emissions



## Benzene Exposures



Note: A comparison of benzene emission sources and benzene exposure sources (home sources include paints and petroleum products; personal activities include driving and use of consumer products that contain benzene. Data taken from Wallace et al. 1991.

Virtually all (99.9%) of the benzene released into the environment finally distributes itself into the air. The general population may be exposed to benzene through inhalation of contaminated air, particularly in areas of heavy motor vehicle traffic and around gas stations. Compared to inhalation, dermal exposure probably constitutes a minor portion of benzene exposure for the general population. Personal sources account for 18% of the total exposure of the general population to benzene. The main personal sources (other than smoking cigarettes) are driving or riding in automobiles and using products that emit benzene (paints, adhesives, marking pens, rubber products, and tapes) (Wallace 1989a).

Benzene constitutes 1-2% of most blends of gasoline and is released as a vapor from vehicular emissions. Since benzene is a constituent of auto exhaust and fuel evaporation, people who spend more time in cars or in areas of heavy traffic have increased personal exposure to benzene. Assuming an average benzene concentration of  $40 \mu\text{g}/\text{m}^3$  (12.5 ppb) for a moving automobile and an exposure duration of 1 hour/day, the calculated intake for driving or riding in an automobile is  $40 \mu\text{g}/\text{day}$  (Wallace 1989a). Pumping gasoline can also be a significant source of exposure. One study reported a benzene concentration of 1 ppm at the breathing-level of a person pumping gas (Bond et al. 1986a). Using this concentration and an estimated 70 minutes/year of time spent pumping gasoline, a benzene intake of  $10 \mu\text{g}/\text{day}$  has been calculated (Wallace 1989a). In an investigation of exposure to methyl *tertiary*-butyl ether (MTBE) in oxygenated gasoline in Stamford, Connecticut, venous blood samples were collected from 14 commuters and from 30 other persons who worked in the vicinity of traffic or automobiles. In addition to MTBE, the samples were analyzed for five chemicals, including benzene. Levels of benzene in the blood of 11 nonsmoking men and women commuters ranged from 0.10 to  $0.20 \mu\text{g}/\text{L}$  (ppb). In the blood of three smoking commuters, benzene levels ranged from 0.14 to  $0.58 \mu\text{g}/\text{L}$ . In 13 nonsmoking car repair workers, blood benzene levels ranged from 0.11 to  $0.98 \mu\text{g}/\text{L}$ ; in 8 smoking car repair workers, levels ranged from 0.17 to  $0.67 \mu\text{g}/\text{L}$ . Three nonsmoking male gasoline attendants had blood benzene levels ranging from 0.32 to  $0.47 \mu\text{g}/\text{L}$  (White et al. 1993). Gasoline vapors vented into the home from attached garages can also increase indoor air exposure to benzene (Wallace 1989a, 1989b). Depending on airflow from garage to living areas, mean indoor benzene concentrations in houses with a garage were 2-5 times higher than outdoor levels in most homes (Thomas et al. 1993). Benzene levels in four garages during different times in a day ranged from 3 to  $196 \mu\text{g}/\text{m}^3$ . The higher concentrations of benzene in these garages were not only from vehicular activity, but also in varying proportions from stored gasoline, paints, and benzene-containing consumer products (Thomas et al. 1993). Inhalation exposure to off-gassing from benzene-containing

products and to evaporative emissions from automobiles in attached garages has been estimated to be 150 µg/day (Wallace 1989a).

All outdoor sources, including automobile exhaust and stationary source emissions, account for only about 20% of the total population exposure to benzene (Wallace 1989b). The main outdoor source is likely to be automobile exhaust (Wallace 1995). Average air intake of benzene for urban/suburban residents (assuming a typical concentration range of 2.8-20 ppb and an intake of 20 m<sup>3</sup> air/day) is 180-1,300 µg/day .

Another source of exposure to benzene for the general population is the use of domestic wood stoves. It has been estimated that approximately 10% of the space heating in urban areas of the northern United States is from wood burning, with up to 50% in smaller, rural towns (Larson and Koenig 1994). Benzene has been found to be a major component of the emissions from wood burning, especially from efficient flame combustion, and constituted roughly 10-20% by weight of total nonmethane hydrocarbons (Barrefors and Peterson 1995). It should be noted, however, that chimney emissions result in much lower human exposure than equally large emissions at the ground level.

Other sources of inhalation exposure to benzene include air around hazardous waste sites, industrial facilities, off-gassing from particle board, and off-gassing from contaminated water during showering and cooking. Based on the TEAM study findings, it appears that the following are not important sources of exposure to benzene on a nationwide basis: chemical manufacturing facilities, petroleum refining operations, oil storage tanks, drinking water, food, and beverages (Wallace 1989a).

Average water intake of benzene (assuming a typical drinking water concentration of 0.1 ppb and a consumption of 2 L/day) is 0.2 µg/day (HSDB 1996). According to another estimate, the daily intakes of benzene for a non-smoking individual (not exposed to secondary smoke) are 1-550 µg (Fishbein 1992).

Individuals employed in industries that use or make benzene or products containing benzene may be exposed to the highest concentrations of benzene. The National Occupational Exposure Survey (NOES), conducted by NIOSH from 1981 to 1983, estimated that approximately 272,300 workers employed in various professions were potentially exposed to benzene in the United States. Approximately half of these workers were employed in general medical and surgical hospitals, and

their occupations included nurses and aides, physicians, technicians, technologists, therapists, dietitians, pharmacists, and janitors (NIOSH 1989). The NOES database does not contain information on the frequency, concentration, or duration of exposure; the survey provides only estimates of workers potentially exposed to chemicals in the workplace. The current OSHA permissible limit for an 8-hour TWA exposure to benzene is 1 ppm and a short-term exposure limit in any 15-minute period is 5 ppm (OSHA 1987a). The NIOSH recommended exposure limit is 0.1 ppm for an 8-hour TWA and 1 ppm for short-term exposure (NIOSH 1992b). In 1987, OSHA estimated that approximately 238,000 workers were exposed to benzene in seven major industry sectors, including petrochemical plants, petroleum refineries, coke and coal chemicals, tire manufacturers, bulk terminals, bulk plants, and transportation via tank trucks (Table 5-3) (OSHA 1987b). Approximately 10,000 workers were estimated to be exposed to TWA concentrations in excess of the 1 ppm standard. This estimate did not include firms covered by the exclusions, firms under jurisdiction of other agencies, or firms involved in the use of products containing small quantities of benzene. The uptake of benzene by workers in a municipal waste incinerator in Germany was assessed by measuring benzene levels in blood (Angerer et al. 1991). No significant difference ( $p < 0.05$ ) in blood benzene levels between workers and controls were detected (mean 0.22  $\mu\text{g/L}$  for non-smoking workers versus 0.25  $\mu\text{g/L}$  for non-smoking controls). OSHA requires the use of engineering controls and/or respiratory protection *in situations* where compliance with the TWA is not feasible (OSHA 1987b).

## 5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Other than individuals who are occupationally exposed, discussed in the preceding section, populations exposed to higher than background concentrations of benzene in the air include those living near certain chemical manufacturing sites, cigarette smokers, passive smokers, and individuals living near hazardous waste sites. Individuals who live near hazardous waste sites or near leaking underground fuel storage tanks might be exposed to potentially high concentrations of benzene in their drinking water if they obtain tap water from wells located near these sources. In a private residence using gasoline-contaminated groundwater (approximately 300  $\mu\text{g/L}$  of benzene), a series of experiments was performed to assess potential benzene exposures that might occur in various parts of the home during a 20-minute shower. Maximum benzene concentrations were observed in the shower stall (758-1,670  $\mu\text{g/m}^3$ ) (237-523 ppb) and bathroom (366-498  $\mu\text{g/m}^3$ ) (115-156 ppb) during and immediately after the shower. The total benzene dose resulting from the shower was estimated to be

**Table 5-3. Percentage of Employees Exposed to Benzene by Exposure Level and Industry Division<sup>a</sup>**

Industry sector	Percentage of observations in each exposure category according to range of 8-hour TWA benzene concentrations (ppm)						Total number of employees
	0.0–0.1	0.11–0.5	0.51–1.0	1.1–5.0	5.1–10	10+	
Petrochemical plants <sup>b</sup>		74.6		23.0	2.4	0.0	4,300
Petroleum refineries <sup>c,d</sup>	64.6	26.1	4.6	3.8	0.5	0.4	47,547
Coke and coal chemicals <sup>e</sup>	0.0	39.3	27.6	27.5	4.4	1.3	947 <sup>f</sup>
Tire manufacturers <sup>c</sup>	53.4	37.5	6.3	2.8	0.0	0.0	65,000
Bulk terminals <sup>c</sup>	57.8	32.8	5.3	3.7	0.3	0.1	27,095
Bulk plants <sup>c</sup>	57.8	32.8	5.3	3.7	0.3	0.1	45,323
Transportation via tank truck <sup>c</sup>	68.4	23.1	5.3	2.9	0.1	0.2	47,600
Total							237,812

<sup>a</sup> Derived from OSHA 1987b

<sup>b</sup> Percentages represent the portion of workers whose average exposures are in each category.

<sup>c</sup> Percentages represent the portion of sampling results in each category.

<sup>d</sup> Data do not reflect respirator use and sampling biases.

<sup>e</sup> Percentages represent the portion of workers whose average exposures are in each category.

<sup>f</sup> Excludes workers employed at the coke ovens.

TWA = time-weighted average

approximately 281 µg, with 40% via inhalation and 60% via the dermal pathway (Lindstrom et al. 1993).

The major source of exposure to benzene is cigarette smoke. A smoker of 32 cigarettes per day (the U.S. average per smoker) would have a benzene intake of approximately 1.8 mg/day (at least 10 times the average nonsmoker's intake) (Wallace 1989a). Median benzene concentrations in 343 homes with smokers averaged 3.3 ppb compared to 2.2 ppb in 185 homes without smokers. This represents a 50% increase in benzene exposure for nonsmokers exposed to passive smoke compared to nonsmokers not exposed to passive smoke (Wallace 1989a).

## 5.7 ADEQUACY OF THE DATABASE

Section 104(I)(5) of CERCLA directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of benzene is available. Where adequate information is not available, ATSDR, in conjunction with NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of benzene.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce or eliminate the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

### 5.7.1 Identification of Data Needs

**Physical and Chemical Properties.** The physical and chemical properties of benzene are well characterized and allow prediction of the transport and transformation of the compound in the environment.

**Production, Import/Export, Use, and Release and Disposal.** In 1994, benzene was the 17th highest volume chemical produced in the United States, compared to the 18th and 17th ranks in 1993 and 1992, respectively (C&EN 1994; Kirschner 1995; Reisch 1994). In 1994, the U.S. production volume of benzene was 14.7 billion pounds (C&EN 1995). The production volume during the 1984-94 period has increased by 4% annually (C&EN 1995). Preliminary production data reported for the first and second quarters of 1995 indicate that this trend will continue; (3.8 billion L [7.4 billion pounds] produced) (USITC 1995). Imports of benzene into the United States have generally ranged from 387 to 729 million pounds during 1990-94 (USDOC 199). Exports decreased from 560 million pounds in 1990 to 6.4 million pounds in 1993 but increased to 115 million pounds in 1994 (USDOC 199). The major use of benzene is in the production of other chemicals (primarily ethylbenzene, cumene, and cyclohexane), accounting for approximately 91% of benzene production volume. Benzene is also used in chemical laboratories as a solvent and a reactant (OSHA 1977, 1987b), as an anti-knock agent in unleaded gasoline (Brief et al. 1980; EPA 19858). The widespread use of benzene as a solvent has decreased in recent years. Many products that used benzene as a solvent in the past have replaced it with other organic solvents; however, benzene may still occur as a trace impurity in these products. Less than 2% of the amount of benzene produced is used as a solvent in such products as trade and industrial paints, rubber cements, adhesives, paint removers, artificial leather, and rubber goods. Benzene has also been used in the shoe manufacturing, and rotogravure printing industries (EPA 1978b; Farm Chemical Handbook 1993; OSHA 1977). In the past, certain consumer products (such as some paint strippers, carburetor cleaners, denatured alcohol, and rubber cement used in tire patch kits and arts and crafts supplies) contained small amounts of benzene (Young et al. 1978). Other consumer products that contained benzene were certain types of carpet glue, textured carpet liquid detergent, and furniture wax (Wallace et al. 1987). The use of benzene in certain pesticides has been canceled. Benzene-containing wastes, such as commercial chemical products, manufacturing chemical intermediates, and spent solvents, are subject to federal and/or state hazardous waste regulations (HSDB 1996). Currently, the recommended method of disposal is to incinerate solvent mixtures and sludges at a temperature that ensures complete combustion. No additional information on the production, import/export, use, release, or disposal of benzene is needed at this time.

**Environmental Fate.** Benzene released to the environment partitions mainly to the atmosphere (Mackay and Leinonen 1975). However, the compound can also be found in surface water and groundwater. Benzene is mobile in soil (Karickhoff 1981; Kenaga 1980); however, there is a need for more information on the leachability potential of benzene to groundwater in different soil types.

Benzene is transformed in the atmosphere by photooxidation. Biodegradation, principally aerobic, is the most important fate process of benzene in water (Delfino and Miles 1985; McAllister and Chiang 1994; Salanitro 1993) and soil (Gibson 1980; Hopper 1978; Salanitro 1993). Benzene can persist in groundwater. No additional information on the environmental fate of benzene is needed at this time.

**Bioavailability from Environmental Media.** Benzene can be absorbed following oral exposure (Thienes and Haley 1972), dermal exposure (Blank and McAuliffe 1985; Franz 1984; Laitinen et al. 1994; Lindstrom et al. 1993; Loden 1986; Susten et al. 1985), and inhalation exposure (Ashley et al. 1994; Avis and Hutton 1993; Boogaard and van Sittert 1995; Brunnemann et al. 1989; Byrd et al. 1990; Etzel and Ashley 1994; Fustinoni et al. 1995; Ghittori et al. 1995; Gordian and Guay 1995; Hajimiragha et al. 1989; Hanzlick 1995; HazDat 1996; Karacic et al. 1995; Kok and Ong 1994; Lagorio et al. 1994a; Laitinen et al. 1994; Lauwerys et al. 1994; Lindstrom et al. 1993; Mannino et al. 1995; Nomiyama and Nomiyama 1974a; Ong et al. 1994, 1995; Pekari et al. 1992; Popp et al. 1994; Rauscher et al. 1994; Rothman et al. 1995; Ruppert et al. 1995; Scherer et al. 1995; Shamy et al. 1994; Srbova et al. 1950). These routes of exposure may be of concern to humans because of the potential for benzene to contaminate the air (Allen 1987; Bennett 1987; Black et al. 1980; Brief et al. 1980; Edgerton and Shah 1992; EPA 1989e; Glass et al. 1986; Graedel 1978; Mangino and Jones 1994; Mayer et al. 1994; TRI93 1995; Wallace 1989a, 1989b; Wallace and Pellizzari 1986; Wester et al. 1986; Wood and Porter 1987), drinking water (CDC 1994; EPA 1979a), and soil (HazDat 1996; Mushrush et al. 1994; TRI93 1995). Information on inhalation exposure and on the absorption of benzene following ingestion of plants grown in contaminated environments near hazardous waste sites would be helpful in determining bioavailability of the compound in these media.

**Food Chain Bioaccumulation.** Benzene has an estimated low-to-moderate bioconcentration potential in aquatic organisms (Miller et al. 1985; Ogata et al. 1984) and some plants (Geyer et al. 1984). Most of the benzene accumulation on vegetation results from air-to-leaf transfer. Root uptake is not believed to be important (Hattemer-Frey et al. 1990). Biomagnification in aquatic food chains does not appear to be important (Ogata et al. 1984). No further information is needed.

**Exposure Levels in Environmental Media.** Benzene is widely distributed in the environment and has been detected in air (EPA 1987e), water (Sauer 1981), soil (EPA 1979a; Ferrario et al. 1985; Staples et al. 1985), sediment, and some foods (EPA 1980b, 1982e). The levels of benzene in air and water are well documented, but there is a need for more current information. Benzene is not expected

to be a significant contaminant in aquatic foods (Geyer et al. 1984; Gossett et al. 1983; Miller et al. 1985; Ogata et al. 1985); however, some contamination of food crops consumed by humans may occur, primarily from air-to-leaf transfer (Hattemer-Frey et al. 1990). The total concentration of benzene on exposed food crops consumed by humans was estimated to be 587 ng/kg (Hattemer-Frey et al. 1990). Humans are at risk of exposure to benzene because of its widespread distribution in the environment, particularly in the atmosphere. Releases to the air from gasoline, smoking, and automobile exhaust constitute the major risk of potential exposure for the general population (Wallace 1995). Additional data characterizing the concentration of benzene in drinking water, air, and soil surrounding hazardous waste sites would be helpful in assessing human exposure for populations living near these waste sites. In addition, more current data on levels of benzene in foods would be helpful in estimating intake of benzene from food.

**Exposure Levels in Humans.** Benzene has been detected in human body fluids and tissues such as blood, urine, and fat (Brugnone et al. 1989; Chao et al. 1993; Karacic et al. 1987). Most of the monitoring data have come from occupational studies of specific worker populations exposed to benzene (Inoue et al. 1989; Karacic et al. 1987; OSHA 1987b). Biological monitoring studies exist for the general population (Melikian et al. 1994). There is information for background levels in breath of smokers and nonsmokers (Wallace 1989b), baseline blood levels (Karacic et al. 1987), and levels of urinary metabolites in unexposed people (Inoue et al. 1989). Information on exposure levels for populations living in the vicinity of hazardous waste sites would be helpful in estimating exposure in these groups. This information is necessary for assessing the need to conduct health studies on these populations.

**Exposure Registries.** In 1995, 1,142 people were included in the Benzene subset of the Volatile Organics Compounds subregistry of the National Exposure Registry. These people were exposed to benzene at a site in Texas. Demographic and health information was obtained on all the exposed persons; the information will be updated longitudinally. For those who were identified as exposed and were deceased, a death certificate will be obtained to ascertain cause of death. This activity is carried out by the Exposure and Disease Registry Branch (EDRB), Division of Health Studies (DHS), ATSDR. The data will become part of public-user data files maintained by ATSDR. The statistical analyses of the baseline data were scheduled to be completed and published, and the CD-ROM released in 1995 (Burg and Gist 1995). The information that is amassed in the National Exposure

Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to the exposure to this substance.

### 5.7.2 Ongoing Studies

As part of the Third National Health and Nutrition Evaluation Survey (NHANES III), the Environmental Health Laboratory Sciences Division of the Center for Environmental Health and Injury Control, Centers for Disease Control and Prevention, will be analyzing human blood samples for benzene and other volatile organic compounds. These data will give an indication of the frequency of occurrence and background levels of these compounds in the general population.

The Federal Research in Progress (FEDRIP 1996) database provides additional information obtainable from a few ongoing studies that may fill some of the data needs identified in Section 5.7.1. New methods for the remediation of groundwater and soil contaminated by benzene are being investigated by A.M. Anderson of University of California, Riverside, California; L.J. Fischer of Michigan State University, East Lansing, Michigan; J.W. Tester of M.I.T., Cambridge, Massachusetts; and M. Tomkiewicz of Brooklyn College, Brooklyn, New York. D.R. Lovely of the University of Massachusetts, Amherst, Massachusetts, is investigating hydrological, geochemical and microbiological controls on anaerobic degradation of aromatic hydrocarbons (including benzene) in petroleum-contaminated groundwater. A high-efficiency activated carbon for removing benzene from drinking water is being developed by R. Mieville of Mega-Carbon, Mt. Prospect, Illinois. The kinetics of vapor phase transport of benzene in soils under natural and forced air advection is being studied by L.M. Abriola of Michigan State University, East Lansing, Michigan. Properties of organic compounds and of soils that govern how aging soil affects bioavailability are being determined by M. Alexander of Cornell University, Ithaca, New York. Several studies are being conducted to investigate the kinetics of biodegradation of benzene under different conditions and to apply this information to the development of bioreactors capable of removing benzene from water and from subsurface aquifers (P.J. Alvarez of the University of Iowa, Iowa City, Iowa; B.R. Folsom of Envirogen Inc., Lawrenceville, New Jersey; J.S. Herman of University of Virginia, Charlottesville, Virginia; J.R. Hunt of University of California, Berkeley, California; N.G. Love of Virginia Polytechnic Institute, Blacksburg, Virginia; R.H. Olsen, J.M. Tiedje, and W.J. Weber of Michigan State University, East Lansing, Michigan; K.F. Reardon of Colorado State University, Fort Collins, Colorado). H. Wijmans of Membrane Technology and Research, Inc., is developing a membrane module for a natural gas

dehydration process to eliminate benzene emissions. Methods are being developed to validate the feasibility of using new biomarkers as a measure of exposure to benzene (D.L. Eaton of University of Washington, Seattle, Washington; A.A. Melikian of American Health Foundation, Valhalla, New York; M.T. Smith and J.H. Weincke of University of California, Berkeley, California). The bioaccumulation potential of benzene in fish from natural bodies of water with contaminated sediments and the relative importance of dietary versus aqueous exposure to benzene are being investigated by W.H. Clements of Colorado State University, Fort Collins, Colorado.

No other ongoing studies for benzene were located.